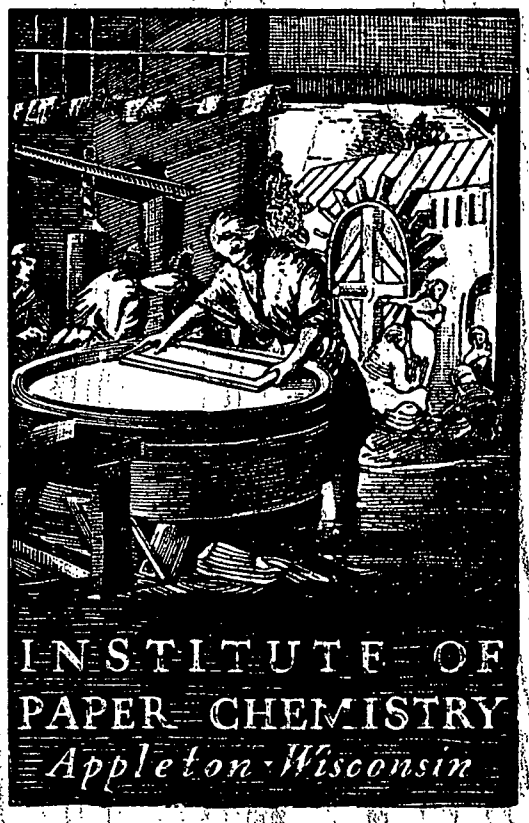

STUDIES ON THE FACTORS GOVERNING RETENTION AND EFFECTIVENESS OF STARCH XANTHATES AND XANTHIDES BY WOOD PULP IN PAPERMAKING

Project 2580

Report Three

A Quarterly Report

to

AGRICULTURAL RESEARCH SERVICE
UNITED STATES DEPARTMENT OF AGRICULTURE

June 17, 1966

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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SUMMARY

The critical or rate-controlling step for retention of starch xanthide probably occurs during the cross-linking reaction. Starch xanthate has not been found to be absorbed by bleached softwood kraft fibers and extending the sorption period after cross-linking did not change the properties of handsheets significantly.

Starch xanthide formed in the presence of fines-free bleached softwood kraft fibers produces excellent improvement in handsheet strength properties with remarkably little slowing of the stock.

Further investigation of the cross-linking reaction discloses an overall production of acidic materials, probably from xanthation by-products. The lowest hypochlorite requirement is found with large amounts of potassium iodide or with a phosphate buffer to protect the system from excursions above approximately pH 7. Competing reactions and the influence of pH are discussed.

INTRODUCTION

This is the third quarterly report submitted to the Agricultural Research Service describing our efforts to achieve the goals of this project. The work covered is in three separate areas of investigation which are separated for clarity and ease of presentation.

The project was established to obtain the basic information that discloses the mechanisms governing the retention of starch xanthate and starch xanthide in paper made from fines-free bleached softwood kraft fibers. This is to be accomplished by observing the sorption rate as a function of such variables as temperature and ionic environment. The initial experiments eliminate sorption of starch xanthate as a significant factor in the retention of starch xanthide in paper. This has focused our attention upon the reaction for the oxidative cross-linking of starch xanthate to form starch xanthide and upon the period after cross-linking.

EXPERIMENTAL

DETECTION OF STARCH XANTHATE IN PAPER

Introduction

The data of Reports One and Two indicate that no significant amount of starch xanthate is retained by cellulose fibers under the experimental conditions described in Report One. This observation is important to the development of mechanisms for starch xanthide retention. It was, therefore, desirable to establish that the lack of retention is due to a lack of sorption by the fiber and not to unsuitable methods of analysis.

There was little reason to suspect the iodine colorimetric method of Browning, Bublitz, and Baker (1) used in Report One. Suitable calibration curves were obtained and a similar method is used to determine the concentration of starch xanthate solutions (2). However, unexpected behavior of starch xanthate could affect the results. A direct assessment of known amounts of xanthate in paper was made to resolve the question.

Experimental

Xanthate Solution

Starch xanthate provided by the cooperator (Run no. 426) was diluted to contain 5.00, 2.50, 1.00, 0.50, and 0.25 grams xanthate starch per 100 grams solution. These solutions were neutralized to pH 7 with dilute acetic acid.

Base Paper

The paper was obtained from a roll of rag-content base paper which is used for the evaluation of surface sizes. The dry weight of the individual 7 by 12-in. sheets was obtained to the nearest 0.01 gram.

Application of Starch Xanthate to the Base Paper

The paper strips were dipped into the xanthate solutions and squeezed between the rubber rolls of a hand-operated clothes wringer. The weight of the wet sheet was determined immediately. Xanthate starch pick-up could then be estimated from the product of the weight gain times the starch xanthate concentration divided by the dry weight of the unsized sheet. Each set of four sheets prepared from each xanthate solution was air-dried at room temperature before being submitted for analysis.

Analysis

The starch xanthate was extracted from the samples with dilute acid and treated with iodine solution. The optical density of the blue-colored aliquot is related to concentration through a standard curve prepared from known concentrations of xanthate starch. Details of the procedures may be found in the paper by Browning, Bublitz, and Baker (1).

Results

The data are presented in Table I.

Total Starch Reported Iodometrically and Bursting Strengths are the averages of duplicate determinations made on each sheet. Figures for xanthate

TABLE I

XANTHATE STARCH DETERMINATIONS

Sheet Number	Xanthate Starch Solution Applied, g./100 g. Solution	Xanthate Starch From Wet Pick-Up		Total Starch Reported Iodometrically		Xanthate Starch Iodometric (Sample minus base), g./100 g. sheet	Burst	
		g./100 g. base	Range	g./100 g. Sheet	Range of Duplicates		Points	Range of Duplicates
Base		0		3.72	0.19	0	30.5	4.0
1	5.0	3.46		5.76	0.25	2.04	45.5	5.0
2		3.42		6.02	0.37	2.30	43.5	1.0
3		3.16		6.08	0.14	2.36	45.8	0.5
4		2.81		6.38	0.17	2.66	44.0	1.0
$\bar{x}$		3.28	0.65	6.06	0.24	2.34	44.7	1.9
5	2.5	1.72		5.62	0.28	1.90	45.0	0
6		1.66		5.49	0.26	1.77	45.0	2.0
7		1.65		5.36	0.25	1.64	46.2	2.5
8		1.57		5.66	0.11	1.94	43.2	0.5
$\bar{x}$		1.65	0.15	5.53	0.22	1.81	44.8	1.2
9	1.0	0.73		4.50	0.04	0.78	37.8	2.5
10		0.75		4.80	0.09	1.08	39.0	2.0
11		0.68		4.89	0.30	1.17	38.5	3.0
12		0.75		4.22	0.23	0.50	38.2	3.5
$\bar{x}$		0.73	0.07	4.60	0.16	0.84	38.4	2.8
13	0.5	0.38		3.87	0.22	0.15	36.5	1.0
14		0.37		4.02	0.22	0.30	39.5	1.0
15		0.38		4.25	0.06	0.53	37.2	1.5
16		0.36		3.82	0.01	0.10	37.0	4.0
$\bar{x}$		0.37	0.02	4.00	0.13	0.30	37.6	1.8
17	0.25	0.19		3.54	0.03	-0.18	38.5	0
18		0.19		3.58	0.33	-0.14	37.5	1.0
19		0.20		3.86	0.33	+0.14	34.5	1.0
20		0.19		3.88	0.44	+0.16	37.2	4.5
$\bar{x}$		0.19	0.01	3.72	0.28	-0.02	37.0	1.6

starch reported are the difference between the Total Iodometric Starch in the sample and in the base sheet.

The analyst noted difficulty in dispersing the samples for starch extraction. Also, it was necessary to centrifuge the filtrates to remove a haze in order to obtain clear aliquots suitable for colorimetry. These problems probably contributed to the greater-than-normal range between duplicates. The age of the samples when analyzed may have contributed to these difficulties. The work schedule of the Analytical Chemistry Group caused a delay of about one month. However, it is more likely that mineral filler and wet-strength resin were present in the base sheet obtained from a commercial source to cause the haziness and persistence of the paper structure.

Discussion

Xanthate starch is found iodometrically in all but the lowest application. However, the unexpectedly large amount of starch in the base sheet and the unusually wide range of the duplicate determinations combine to make the results of the next lowest application of doubtful significance.

The data for the remaining three samples are consistent in showing higher levels present with higher concentrations applied. The agreement between the two methods of estimating starch added is less than could be desired.

The question to be answered, however, is whether starch xanthate in paper can be detected by the method of Browning, Bublitz, and Baker. These data support the belief that at least 1% starch xanthate on the weight of the paper can be observed by this method. On this basis it can be stated that if starch

xanthate is absorbed by bleached kraft fibers under the conditions described in Report One, less than 1% is absorbed since equal amounts of xanthate and fiber were present in the sorption media.

The burst data were obtained as an indirect check on the starch analyses. It appears that starch xanthate is an effective tub size. The difference between the base sheet and the lowest xanthate level, is probably due to the latter having a higher basis weight due to unrestrained shrinkage during air drying.

STARCH XANTHIDE IN FINES-FREE BLEACHED KRAFT HANDSHEETS

Introduction

The preparation of handsheets containing starch xanthide was undertaken to determine some of the effects of this additive upon paper made with the pulp selected for this project. This information would serve as a base line for comparison with subsequent developments.

An opportunity was also provided to observe the procedure for making starch xanthide in the presence of wood fiber and to test the effects of controlled variations of the procedure.

The basic methods will be described first. Subsequent modifications are discussed in the separate parts of this section.

Experimental

Preparation of Pulp

Rayonier western softwood bleached kraft pulp was beaten to 700 Schopper-Riegler freeness in deionized water and processed in a Bauer-McNett

classifier. The material passing the 150-mesh screen was discarded. Fibers rejected by the 12, 20, 65, and 150-mesh screens were combined, dewatered, given three passes through a pulp breaker, blended, and stored under refrigeration in polyethylene bags. The fines-free pulp has a Schopper-Riegler freeness of 860-870.

Starch Xanthate

The starch xanthate was prepared by the cooperator (Run Number 428) on April 25, 1966 and used the following two weeks. Dilution to 5% as starch was based on the information provided with the sample (9.61 g. starch/100 g. solution, D.S. = 0.125).

Sodium Hypochlorite

A commercial household bleach (Hi-lex) was diluted to approximately 1% sodium hypochlorite (pH 11.4) by fivefold dilution with deionized water. The original concentration was subsequently found to be 5.57% NaOCl.

Handsheet Preparation

The procedure developed at Peoria was followed as closely as possible (3).

The pulp (25.0-g. dry basis) was dispersed 2-1/2 minutes in a British disintegrator at 2% consistency in deionized water (1 to 2 x 10^6 Ohm resistance). Starch xanthate was added to the stock (17° to 20°C.) and blended with the fiber for 5 minutes by vigorous agitation with a laboratory Lightnin' mixer. The pH of the mixture was adjusted to about 10 with 20% acetic acid before alum (10%, by wt.) was added to give 2% $Al_2(SO_4)_3 \cdot 18H_2O$ on the fiber. Further adjustment

to pH 5.5 was made with dilute acetic acid or sodium hydroxide as required. One milliliter of 10% potassium iodide was pipetted into the stock immediately before starting the addition of sodium hypochlorite from a 50-ml. buret (120-sec. drainage time). The appearance of the blue starch – iodine color, indicating a small excess of sodium hypochlorite, was the criterion for discontinuing the addition of hypochlorite. No adjustment of pH was made during or after this addition.

Agitation was stopped within approximately 10 seconds of the appearance of the blue color and the mixture was allowed to stand for one minute before dilution to 0.5% consistency. The diluted stock was stirred an additional four minutes before starting to make the handsheets.

Handsheets were formed at 0.04% consistency in deionized water (13° to 16°C.) in an 8-inch by 8-inch Noble and Wood sheet mold equipped with a one-hundred mesh Monel wire. The 2.5-gram handsheets were pressed between blotters at 50 pounds per square inch for 5 minutes and dried on single blotters for seven minutes on a drum containing steam at 3.5 pounds per square inch gage pressure.

Testing

The handsheets were preconditioned to 14% R.H. at 73°F. before conditioning and testing at 50% R.H. at 75°F. Basis weight (24 x 50/500), caliper, apparent density, Mullen, fold (M.I.T.), dry tensile strength (Instron), and wet tensile strength (Schopper, 30-minute soak) were determined according to Institute procedureswhich are similar to the TAPPI Standard Procedures. Xanthide content was determined by an adaptation of the procedure of R. A. Buchanan (4).

The samples were ground (Wiley Mill, 20-mesh screen) in order to improve the precision of the extraction and hydrolysis steps. Even so we are not satisfied with the precision we have obtained. A portion of the hydrolyzate was centrifuged and analyzed for reducing sugar by colorimetric determination of reduced copper following an alkaline copper sulfate reaction (5). The results are reported as grams anhydroglucose per 100 grams ovendry paper.

Effect of Xanthate Addition Level

Experimental

Three replications of 0, 5, 10, 20, and 40% starch xanthate additions based on the dry fiber weight were made using the basic procedure.

Results

The data obtained are presented in Table II.

Discussion

A few peculiarities were observed during the preparation of the xanthide. One is that the amount of hypochlorite added to obtain the blue color does not have a predictable effect upon the pH of the stock. A small rise is expected since sodium hydroxide as well as sodium hypochlorite is present in the Hi-lex solution. The pH is higher but varies from 0.3 to 1.5 units higher without any consistent relationship to the quantity of hypochlorite added. The greatest average higher pH occurred with the 20% xanthate preparation rather than with 40% xanthate.

TABLE II

REPLICATION OF STANDARD XANHIDE PROCEDURE WITH FINES-FREE BLEACHED KRAFT

Hand-sheet Set No.	Xanthate, parts/100 parts fiber	1% NaOCl (pH 11.4), ml.		Stock pH		0.5% Consistency	Sheet Mold	Basis Wt., lb. (25 x 40/500)		Caliper, 0.001 in.	Apparent Density, lb./0.001 in.		Burst, pts./100 lb.		M.I.T. Fold, double folds		Dry Tensile (Instron), lb./in.		Wet Tensile (Schopper), lb./in.		Xanthide Content, % sheet wt.
				Before NaOCl	After NaOCl																
(N)		$\bar{x}$	C.I.	$\bar{x}$ C.I. (1)	$\bar{x}$ C.I. (1)	$\bar{x}$ C.I. (1)	$\bar{x}$ C.I. (1)	$\bar{x}$	(1)	(8)	$\bar{x}$	C.I. (--)	$\bar{x}$	C.I. ($\bar{5}$)	$\bar{x}$	C.I. ($\bar{10}$)	$\bar{x}$	C.I. ($\bar{5}$)	$\bar{x}$	C.I. ($\bar{5}$)	$\bar{x}$
114-1	0	0		5.5	--	5.8	6.2	45.8	x	4.9	9.3		88		428		17.5		0.80		--
114-6	0	0		5.6	--	5.6	6.2	44.3		4.8	9.2		77		413		16.8		0.69		--
114-11	0	0		5.5	--	5.7	6.6	43.8		4.8	9.1		84		431		16.8		0.70		0
$\bar{x}$	0	0		5.5		5.7	6.3	44.6		4.8	9.2	0.2	83	10	424	16	17.0	0.6	0.73	0.10	--
114-2	5	5.6		5.6	6.7	6.5	6.7	43.5		4.6	9.5		136		1690		23.3		2.3		--
114-7	5	5.9		5.2	5.6	5.6	5.9	43.6		4.7	9.3		132		1340		23.9		1.8		--
114-12	5	5.4		5.5	6.1	6.0	6.2	43.8		4.7	9.3		140		1570		24.4		2.4		1.1
$\bar{x}$	5	5.6	0.4	5.4	6.1	6.0	6.3	43.6		4.7	9.4	0.2	136	7	1533	312	23.9	1.0	2.2	0.5	--
114-3	10	11.5		5.3	5.8	5.7	6.0	45.5		4.7	9.7		149		2330		28.4		4.1		--
114-8	10	11.9		5.4	5.8	5.8	6.1	46.5		4.8	9.7		148		2170		29.5		3.6		--
114-13	10	12.5		5.5	5.8	5.7	6.0	41.4		4.4	9.4		151		1560		26.3		2.9		1.2
$\bar{x}$	10	12.0	0.9	5.5	5.8	5.7	6.0	44.5		4.6	9.6	0.3	149	3	2020	678	28.1	2.8	3.5	1.1	--
114-4	20	22.5		5.5	6.7	7.0	6.7	44.2		4.5	9.8		158	10	2710	281	29.8	1.1	4.8	0.4	--
114-9	20	22.2		5.5	7.4	7.0	6.8	44.5		4.5	9.9		149	11	2580	213	32.1	2.1	4.8	0.5	--
114-14	20	25.0		5.5	7.0	6.7	6.6	45.2		4.4	10.3		174	23	2550	355	28.9	2.0	5.2	0.4	4.6
$\bar{x}$	20	23.2	2.5	5.5	7.0	6.9	6.7	44.6		4.5	10.0	0.4	160	22	2613	141	30.3	2.8	4.9	0.4	--
114-5	40	50.0		5.5	7.4	7.1	6.9	45.9		4.7	9.8		99		3530		21.9		6.1		--
114-10	40	67.3		5.5	6.2	6.0	6.2	49.7		4.7	10.6		98		4150		23.7		5.3		--
114-15	40	67.7		5.5	6.1	6.1	6.0	52.0		5.1	10.2		75		3190		19.4		3.7		13.3
$\bar{x}$	40	61.7	15.6	5.5	6.3	6.4	6.4	49.2		4.8	10.2	0.7	91	21	3622	885	21.7	3.8	5.0	1.1	--

C.I. = 90% Confidence interval based on range.

Note: C.I. of each set is based on range of individual observations.
C.I. of means for each xanthate level is based on the range of set means.

In general, increasing amounts of xanthate are accompanied by higher apparent density, burst, fold, dry tensile, and wet tensile. However, bursting and dry tensile strengths are very much lower at 40% xanthate addition than with 20% xanthate. There are fewer fibers per unit weight of the handsheet prepared at the higher addition levels – assuming nearly complete xanthide retention. This could account for the lower burst and tensile values. Another possibility is the large clumps of parallel fibers that formed during the oxidation of the 40% xanthate system. These clumps (about 1 cm. in diameter) persisted into the sheet mold, harming the formation of the handsheets and thereby the strength. This condition is different than the rather randomly oriented clots frequently seen in lightly beaten kraft fibers.

The handsheets became more yellow and more translucent as the xanthate level increased. The latter is to be expected. However, the yellow color is not expected and would be undesirable in commercial operations with bleached fiber.

The good improvement of the test values with as little as 5% xanthate and the remarkable freeness of the stock at 40% xanthate additions are interesting. It is extremely unusual to obtain the highest fold resistance at the highest additive level in a series covering the range used in this study.

The results of the xanthide analyses are disappointing. It was expected that they would be much higher (4). The weight gain of the handsheets made to determine stock consistency, using the same volume and nearly the same fiber concentration as the control sheets, suggested 90 to 100% retention of the xanthide.

Effect of Varying Agitation Period After Adding Sodium Hypochlorite

Experimental

Three more sets of handsheets were prepared using 20% xanthate starch on the fiber. Instead of allowing the stock to stand quietly for one minute after stopping agitation 10 seconds after the appearance of the blue color, stirring was continued for 60, 300, and 600 seconds.

Results

These data are presented in Table III.

Discussion

Extending the agitation period to 60, 300, or 600 seconds has no effect (90% confidence level) upon these handsheets in comparison with the data presented in Table II. The only significant difference appeared in the decreased fold resistance obtained with 600 seconds agitation. A judgment on the xanthide retention is held in abeyance until we gain more experience with this determination.

Since there is a finite time involved in diluting the stock and making the individual handsheets, it is possible that some of the effects of the agitation period are obscured. If a significant amount of xanthide absorption occurs during the time between the completion of cross-linking and when the handsheets are formed, then each handsheet in succession should contain more and more xanthide. This should affect the response of each sheet to the evaluation tests and increase variability thus extending the 90% confidence interval. This effect should decrease as the agitation interval is extended since the difference in sorption time between

TABLE III

EFFECT OF AGITATION TIME

Set no.	114-16	114-17	114-18	Mean
Post xanthide mixing time, sec.	60	300	600	$\bar{x}$ C.I.[b]
1% NaOCl, ml.	20.4	19.5	19.6	19.8 ± 0.7
pH Before NaOCl	5.5	5.5	5.5	5.5 ± 0
After NaOCl	7.7	7.4	6.8	7.3 ± 0.8
0.5% Consistency	6.1	7.5	6.7	6.8 ± 1.2
Sheet mold	6.9	6.9	6.6	6.8 ± 0.3
test data:	$\bar{x}$ ± C.I.[a]	$\bar{x}$ ± C.I.[a]	$\bar{x}$ ± C.I.[a]	
Basis Wt. (25 x 40/500), lb.	42.6	43.7 -	46.2 -	44.2 ± 2.2
Caliper, mils.	4.4	4.4 -	4.6 -	- -
Density, (basis wt./caliper)	9.7	9.9	10.0 -	9.9 ± 0.3
Burst, (pts./100 lb.)	155 4.1	161 16.5	161 9.3	159 ± 5
M.I.T. fold, double folds	2570 206	2610 243	2040 182	2405 ± 501
Dry tensile (Instron), lb./in.	28.8± 1.2	28.2 1.0	28.5 3.0	28.5 ± 0.5
Wet tensile (Schopper), lb./in.	5.4 0.3	5.0 0.3	5.0 0.1	5.1 ± 0.4
Xanthide in sheet, %	4.7	2.6	5.4	--

C.I. = 90% Confidence interval based on range.

[a] C.I. based on range of individual observations.

[b] C.I. based on range of means.

handsheets becomes less significant. Consequently, the 90% confidence interval would be expected to decrease as the agitation period increases from 10 seconds (Table II) to 600 seconds (Table III). The confidence intervals do vary but not in a way clearly attributable to time.

It would seem that xanthide retention is a rather rapid process.

We have no explanation for the lower hypochlorite consumption during the cross-linking step for this set of experiments.

Effect of the pH of the Hypochlorite Solution

Experimental

For convenience, alum was added to the mixture of fiber and 20% xanthate before adjusting to pH 5.5. This eliminates one step.

Hi-lex (100 ml.) was diluted to 400 ml., adjusted to pH 8.5, 7.0, 5.5, or 4.0 with acetic acid before being made up to 500 ml. These solutions were prepared individually within 10 minutes of being used for cross-linking.

The xanthide mixture was stirred for two minutes before dilution to 0.5% consistency.

Results

The data are summarized in Table IV.

Discussion

Hypochlorous acid ($pK_a = 7.2$) is less than 0.1% ionized at pH 4 and about 90% ionized at pH 8.5. On the basis of the similarity in the amount of

TABLE IV

EFFECT OF OXIDANT pH

Set No.	121-1		121-2		121-3		121-4		Mean		123-1	
	$\bar{x}$	C.I.[a]	$\bar{x}$	C.I.[a]	$\bar{x}$	C.I.[a]	$\bar{x}$	C.I.[a]	$\bar{x}$	C.I.[b]	$\bar{x}$	C.I.[a]
NaOCl pH	8.5	--	7.0	--	5.5	--	4.0	--	--	--	11.4	--
1% Hi-lex Used, ml.	23.5	--	25.7	--	23.1	--	24.0	--	24.1	1.4	50.0	(Twofold excess)
pH Before Hi-lex	5.5	--	5.5	--	5.5	--	5.5	--	--	--	5.5	--
After Hi-lex	6.1	--	5.6	--	5.6	--	4.7	--	--	--	7.0	--
0.5% Consistency	6.0	--	5.6	--	5.6	--	4.8	--	--	--	6.9	--
Sheet mold	7.0	--	5.8	--	5.7	--	4.9	--	--	--	6.8	--
Basis wt. (25 x 40/500), lb.	43.3	--	42.8	--	44.2	--	45.1	--	43.8	1.2	44.7	--
Caliper, mils	4.3	--	4.2	--	4.3	--	4.4	--	--	--	4.2	--
Apparent density (basis wt./mil)	10.1	--	10.2	--	10.3	--	10.2	--	10.2	0.1	10.6	--
Burst, pt./100 lb.	180	6	170	7	157	6	169	11	169	12	176	4
M.I.T. Fold, double folds	2820	151	2680	131	3080	285	2950	202	2882	742	3350	335
Dry tensile (Instron), lb./in.	32.4	1.4	32.4	2.5	32.0	2.4	32.9	1.2	32.4	0.2	32.7	2.5
Wet tensile (Schopper), lb./in.	5.7	0.4	4.8	0.3	5.1	0.3	5.0	0.4	5.2	0.4	7.0	0.3
Xanthide in sheet, %	4.1	--	4.8	--	5.3	--	6.6	--	--	--	4.1	--

C.I. = 90% Confidence interval based on range, confidence limits are $\pm$ C.I.

[a] C.I. Based on range of individual observations.

[b] C.I. Based on range of means.

solution required to produce the blue end point, it appears that the degree of ionization is relatively unimportant to the oxidation reactions. The volumes of consumed oxidant adjusted to pH 4.0, 5.5, 7.0, and 8.5 are within the 90% confidence range of the titrations accomplished with hypochlorite at pH 11.4 (Table V).

TABLE V

SUMMARY DATA FROM OXIDANT pH STUDY

Hi-lex pH	Oxidant Consumed, ml.	Burst, pt./100 lb.	M.I.T. Fold	Tensile		Xanthide Content, %
				Dry, lb./in.	Wet, lb./in.	
11.4[a]	23.2 ± 2.5	160 ± 22	2613 ± 141	30.3 ± 2.8	4.9 ± 0.4	4.6
8.5[b]	23.5	180	2830	32.4	5.7	4.1
7.0[b]	25.7	170	2680	32.4	4.8	4.8
5.5[b]	23.1	157	3080	32.4	5.1	5.3
4.0[b]	24.0	169	2950	32.9	5.0	5.6

[a] From Table II.
[b] From Table IV.

Handsheet properties of density, burst, dry tensile, and wet tensile are unaffected by the degree of ionization of the hypochlorous acid used for cross-linking (Table IV). While the wet tensile value obtained for the pH 8.5 set does exceed the confidence interval for the pH 11.4 replications, this difference has little practical significance. While most of the means for the fold test exceed the pH 11.4 confidence interval, it is difficult to assign these results to the effect of the pH of the oxidant solution.

Oxidant pH apparently is unimportant here. However, it must be remembered that hypochlorite decomposes to chlorite and chlorate. These reactions proceed more rapidly near pH 7. Consequently, the concentration of active oxidant decreases with time. We have not been able to effect cross-linking with chlorate in the few experiments we have tried.

It appears that adding alum before neutralizing the xanthate-fiber mixture does not affect the performance of the handsheets. This is probably due to the fact that we can neutralize only to pH 10 when using deionized water to avoid having the pH drop below 5 when the alum is added. That is, the difference between pH 11.7 and pH 10.0 is inconsequential.

Rapid Addition of Excess Hypochlorite

When 50 milliliters of 1% Hi-lex (pH 11.4) is poured rapidly into a pH 5.5 mixture of 20% xanthate and kraft fiber in the presence of potassium iodide, the starch-iodine color does not appear until about one minute afterward. The color changes to purple within another minute and persists through handsheet forming up to the drying step.

The only observable effect upon the handsheets (last column Table IV) is improved wet tensile strength. Apparently, a twofold excess of hypochlorite is not harmful to the handsheet properties tested.

FURTHER INVESTIGATIONS OF THE CROSS-LINKING REACTION

pH Effects

The initial investigations of the hypochlorite oxidation of starch xanthate to starch xanthide were covered in Report Two. This work was continued using the basic procedures described in the earlier report.

It is presumed that the cross-linking reaction is complete when hypochlorite is added in quantities sufficient to produce the blue color of the starch – iodine complex in the presence of a small amount of potassium iodide. We found that, by this criterion, the reaction was not quantitative. Amounts of hypochlorite considerably in excess of those anticipated were consumed erratically. It was not possible to control pH during these reactions. Each increment of hypochlorite elevated the pH immediately. This was followed by a time-dependent asymptotic decline from the initial peak.

The elevation of pH with incremental additions of hypochlorite should accelerate the disproportionation and saponification of xanthate mixtures also encouraged by the oxidative removal of parts of the equilibrium mixture. The formation of hypochlorite-susceptible compounds at the expense of starch xanthate is promoted. Further investigations into the pH effects were undertaken and will be discussed qualitatively.

The overall effect of combining crude starch xanthate solutions and sodium hypochlorite is to lower the pH. When hypochlorite is added to starch xanthate, the "equilibrium" pH decreases with the volume of titrant in a manner resembling a common acid – base titration. At the point excess hypochlorite can be detected by an external indicator (KI on filter paper), the pH rises with further additions. The same behavior is observed when starch xanthate is added to sodium hypochlorite. However, there is little or no time-dependent pH change with each increment of xanthate solution. When hypochlorite can no longer be detected by the external indicator, the pH rises.

The initial pH of the solution being titrated has little effect other than to establish the starting point. That is, adding pH 11.4 xanthate to pH

11.4 hypochlorite decreases the pH of the reaction solution. Adding pH 11.4 xanthate to pH 5.5 hypochlorite also lowers the pH up to the disappearance of hypochlorite. This behavior was simulated by titrating sodium bisulfite with sodium hypochlorite. In this reaction, anions of incompletely ionized acids (HSO_3^-, ClO^-) are converted to anions of fully ionized acids ($SO_4^=$, Cl^-). Consequently, the pH drops until the bisulfite is consumed. After this, the pH rises with further additions of sodium hypochlorite.

The low degree of time dependency for the pH changes after adding starch xanthate to sodium hypochlorite may support the contention that disproportionation and saponification occur in the xanthate system during the relatively slow titrations with hypochlorite. Components in the xanthate mixture added to hypochlorite apparently react rapidly to lower the pH and to stabilize the products so that disproportionation does not occur or does not have an effect upon the pH of the system.

Role of Potassium Iodide

Introduction

In some of the exploratory titrations, it was observed that the blue color of the end-point reaction was not obtained until more potassium iodide was added. Occasionally, the blue color appeared many seconds after the addition of an increment of hypochlorite. These observations revealed the need to examine the role of potassium iodide in the xanthide reaction.

Experimental

Starch xanthate. Run No. 428 (age 26 days) was diluted with deionized water to contain 2.0% by weight as starch. The xanthate D.S. was 0.125 at the time of its preparation.

Sodium hypochlorite. Hi-lex was diluted one volume to five volumes to give a solution containing about 0.16M NaOCl.

1% Potassium iodide. Reagent-grade potassium iodide (10.0 g.) was dissolved in deionized water and made up to 1000 ml.

Procedure. The starch xanthate solution (50-ml., graduate) was adjusted to pH 5.2 to 5.6 with 20% acetic acid before adding 1% potassium iodide from a 50-ml. buret. Sodium hypochlorite was added from a 50-ml. buret with a partially opened stopcock until the blue color of the starch iodine complex appeared in the magnetically stirred solution. The interval between starting the essentially continuous addition of hypochlorite and the appearance of the blue color was measured with an electric timer. A Beckman Model N pH meter, equipped in a molded 41263 glass electrode was used to measure the initial and terminal pH of the xanthate solutions and to observe fluctuations during the titration.

A second series of titrations was conducted with the same amount of xanthate but with 450 ml. deionized water added to give a total volume of 500 ml. or an initial concentration of 0.2% xanthate.

Four titrations were conducted in the presence of 0.50 g. anhydrous K_2HPO_4 dissolved in the xanthate before pH adjustment.

Results

The data are presented in Table VI.

Discussion

When using small amounts of potassium iodide, it is very difficult to stop the addition of hypochlorite before exceeding the amount required to

reach the end point. If excess hypochlorite is added, more iodide must be added to obtain the blue color. It appears that in this experiment, 0.40 ml. (0.4 g. KI per 100 g. xanthate starch) is the smallest amount that can be used.

TABLE VI

EFFECT OF POTASSIUM IODIDE

Initial Concn., %	1% KI ml.	0.16N NaOCl ml.	Addition Time, sec.	pH Initial	pH Final
2.0	0.10	8.60[ab]	109	5.5	6.0
	0.20	10.90[ac]	210	5.5	5.7
	0.40	6.05	50	5.5	6.2
	0.40	7.10[ad]	18	5.4	6.1
	0.40	7.15	117	5.5	6.3
	0.50	6.75	57	5.5	6.4
	1.00	7.50	26	5.2	5.5
	1.00	6.35	93	5.4	6.2
	1.00	6.50	310	5.5	> 7, varied
	10.00	5.00	342	5.4	9.6, dropped to 7.7
0.20	0.50	7.5[a]	<60	5.5	5.5
	1.00	11.50	57	5.5	> 9, dropped to 6.4
	12.60	5.00	<60	4.8	4.9
(0.50 g. K_2HPO_4 added to xanthate solution);					
0.20	1.00	5.20	76	5.4	5.6
2.00	0.40	5.20	69	5.5	5.7
	11.00	4.70	115	5.5	5.7
	20.00	4.60	68	5.4	5.7

[a] Ran past end point.
[b] Precipitate at 7.0 ml.
[c] Precipitate at 7.5 ml.
[d] Precipitate at 6.5 ml.

The smallest amount of hypochlorite is required when at least 10 ml. of potassium iodide is present (10 g. KI per 100 g. xanthate starch).

The general impression is that the amount of potassium iodide present does affect the hypochlorite requirement in the 2% xanthate series without phosphate.

In the series using 0.2% xanthate, the results are erratic and not easily interpreted.

One observation not shown in the table is that starch xanthide did not precipitate in any of the reactions carried out at 0.2% xanthate but did precipitate in every reaction starting with 2.0% xanthate. The 0.2% xanthide reaction mixtures were opalescent but still transparent while the higher concentration produced opaque suspensions of 1 to 2 mm. curds. This probably indicates that concentration is involved in the starch xanthide coagulation process.

The most encouraging results were obtained when a phosphate buffer was used. The hypochlorite requirement is lowest and is relatively unaffected by either the amount of iodide or the xanthate concentration. A dual buffer system (acetic acid – acetate and H_2PO_4 – HPO_4) which confines the excursions of pH during the reaction between approximately pH 5 to 7, probably is required to minimize undesirable side reactions.

However, earlier work at Peoria shows little advantage in using a carbonate buffer (7).

Discussion of Stoichiometry and Side Reactions

The following discussion is based on the experimental work, several standard texts (6, 8, 9, 10, 11) and referral to the general literature.

The conversion of starch xanthate to starch xanthide by the action of sodium hypochlorite is a fundamental step which must be included in the sorption mechanism. A sound understanding is essential in order to develop adequate experimental procedures. Further examination has led to a revision of our concept of the stoichiometry of this reaction (12).

The oldest test (10, p. 999) for xanthate sulfur is the oxidation of cellulose xanthate to cellulose xanthide with iodine. In this reaction the production of one xanthide linkage consumes two atoms of iodine and 2 xanthate groups leaving two iodide ions.

$$2\ RO.CS.S^- + I_2 \longrightarrow (RO.CS.S.)_2 + 2I^- \qquad (1).$$

A similar two-electron transfer reaction is the oxidation of thiosulfate by iodine in acid media, to tetrathionate.

$$2\ SO_3.S^{=} + I_2 \longrightarrow (SO_3.S.)_2^{=} + 2I^- \qquad (2).$$

Tetrathionate can be used to produce xanthides (13).

$$\begin{matrix} RO.CS.S^- \\ RO.CS.S^- \end{matrix} + \begin{matrix} S.SO_3^- \\ S.SO_3^- \end{matrix} \longrightarrow \begin{matrix} RO.CS.S \\ RO.CS.S \end{matrix} + \begin{matrix} {}^-S.SO_3^- \\ {}^-S.SO_3^- \end{matrix} \qquad (3).$$

The equivalence of hypochlorite to iodine is expressed by the following equations which hold in acid media.

$$ClO^- + Cl^- + 2H^+ \longrightarrow Cl_2 + H_2O \qquad (4),$$

$$2I^- + Cl_2 \longrightarrow I_2 + 2Cl^- \qquad (5),$$

$$ClO^- + 2I^- + 2H^+ \longrightarrow I_2 + Cl^- + H_2O \qquad (6).$$

This leads to a stoichiometric relationship somewhat different than visualized in Report Two.

$$2\ RO.CS.S^- + ClO^- + 2H^+ \longrightarrow (RO.CS.S.)_2 + Cl^- + H_2O \qquad (7).$$

According to this representation, one xanthide bond is produced by one hypochlorite ion rather than two. The reaction should raise the pH since hydronium

ions and the base, ClO^-, are consumed in unequal amounts. This is similar to xanthide formation with Chloramine T. Chlorine in this material reacts similarly to hypochlorite in most reactions (13).

$$2\ RO.CS.S^- + CH_3.C_6H_4.SO_2\ (NCl)^- + 2H_2O \longrightarrow (RO.CS.S.)_2 + CH_3.C_6H_4.SO_2\ NH_2 + 2OH^- + Cl^- \qquad (8).$$

This sequence also has a one-to-one relationship of the xanthide bond to chlorine atom and is pH elevating.

The pH of the xanthide reaction mixture is the result of a number of competing reactions. Elevation of pH due to the xanthide reaction is opposed by the production of a strong acid (HCl) from a weak acid (HOCl). In addition, several other reactions are involved that tend to change the pH of the system. One of these, is the decomposition of hypochlorite to chlorate and chloride. Both are stronger acids than hypochlorite.

$$3\ ClO^- \longrightarrow ClO_3^- + 2\ Cl^- \qquad (9).$$

This reaction proceeds most rapidly near pH 7 (6, p. 116).

Sodium cellulose xanthate as normally produced commercially is accompanied by numerous by-products. Among those identified are sodium trithiocarbonate and the products of its hydrolysis and air oxidation: sulfide, perthiocarbonate, and thiosulfate (14). These materials must also exist in starch xanthate solutions. However, if the system is neutralized to pH 5 or 6, sulfide, thiosulfate, and carbon disulfide would be the main sulfur-containing contaminants. These materials are oxidized by hypochlorite.

We have not been able to locate a description in the literature of the action of hypochlorite upon carbon disulfide. However, qualitative observations of this reaction were made at room temperature. Carbon disulfide disappears as a separate phase in the presence of dilute sodium hypochlorite. Heat is produced. A gas, insoluble in the alkaline media, is formed and has an odor like phosgene ($COCl_2$). As the reaction proceeds, the pH drops about to neutrality and a yellow color appears in the as yet unconsumed carbon disulfide. Additional hypochlorite destroys the yellow color. Effervescence occurs upon acidification and precipitation occurs upon the addition of barium chloride. The following incomplete equation is suggested by these observations:

$$CS_2 + ClO^- \longrightarrow SO_4^= + CO_3^= + COCl_2 + Cl^- + S^o + \ldots \qquad (10).$$

Hypochlorite can oxidize the other sulfur by-products to sulfate.

$$S^= + 4\ ClO^- \longrightarrow SO_4^= + 4\ Cl^- \qquad (11),$$

$$S_2O_3^= + 4\ ClO^- + H_2O \longrightarrow 2SO_4^= + 4Cl^- + 2H^+ \qquad (12).$$

When potassium iodide is introduced, the stoichiometry becomes quite pH dependent. Reaction (6) describes the behavior of iodide and hypochlorite in acid media. However, in neutral or slightly acidic media, Reaction (12) becomes significant (11, p. 649).

$$I^- + 3\ ClO^- \longrightarrow IO_3^- + 3\ Cl^- \qquad (13).$$

Iodine is liberated by hypochlorite even in basic solutions. However, the iodine soon disappears.

$$I_2 + 2OH^- \longrightarrow IO^- + I^- + H_2O \quad (14),$$

$$3IO^- \longrightarrow IO_3^- + 2I^- \quad (15),$$

$$I_2 + S^= \longrightarrow S^o + 2I^- \quad (16),$$

$$I_2 + S_2O_3^= \longrightarrow S_4O_6^= + 2I^- \quad (17),$$

$$4I_2 + S_2O_3^= + 10\ OH^- \longrightarrow 2SO_4^= + 8I^- + 5H_2O \quad (18).$$

Reaction (1), of course, also can contribute to the disappearance of hypochlorite released iodine.

The question whether iodine or hypochlorite is the effective cross-linking agent remains open. However, the data in "Role of Potassium Iodide" (p. 22) iodine may be participating (3, p. 2).

The pH changes during the addition of hypochlorite to the reaction mixture demonstrate the inequality of the rates of the acid- and base-producing reactions. A buffering system which limits oscillation of pH in both directions should improve the reproducibility of the reaction by minimizing hypochlorite consumption by unproductive side reactions.

FUTURE WORK

It is our aim to examine xanthide sorption as a function of time starting with the introduction of hypochlorite. In order to do this, we need to be able to predict the amount of hypochlorite necessary to complete the cross-linking reaction so that the hypochlorite and xanthate can be combined rapidly and reproducibly. It appears we are approaching this capability.

Our working hypothesis is that starch xanthide coagulates to form particles (15) which are retained by mechanisms proposed for mineral fillers such as titanium dioxide (16). If this is true, then particle size and distribution will have significant effects upon retention and effectiveness. Details of many of the factors that could be involved are presented in a review by LaMer and Healy (17).

Further work is needed to verify our ability to obtain reproducible hypochlorite consumption and to gain confidence in our ability to analyze for xanthide in paper.

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